

Pyrrolidinium TFSI Ionic Liquid Preparation

Overview:

This procedure involves synthesis and purification of the hydrophobic ionic liquid Pyrrolidinium TFSI from pyrrolidinium and sulfonamide cations. Original Procedure: Arthur Beausoleil (7/17/16)

Background:

This procedure involves synthesis and purification of the hydrophobic ionic liquid Pyrrolidinium TFSI from pyrrolidinium and sulfonamide cations. This procedure (including supply list) is written for 10 ml product at the expected yields below, but can be generalized to other similar ionic liquids at different volumes.

Step 1: Precursor Synthesis

1-iodo-butane + 1-methyl-pyrrolidinium \rightarrow 1-butyl-1methyl-iodo-pyrrolidinium

Step 2: Anionic Exchange

1-butyl-1methyl-iodo-pyrrolidinium + Lithium bis(trifluoromethane)sulfonamide \rightarrow lithium iodide + 1-butyl-1-methyl-pyrrolidinium-bis(trifluoromethane)sulfonamide

During step one, 10%wt excess of Pyr₁ is combined with Iodo Butane, producing product at a typical yield of 83%. Ethyl Acetate solvent is used during this step in a ratio of roughly 2:3 (%vol) reagents:solvent.

During step two, 3%wt excess of LiTFSI is combined with the Pyr₁₄ to produce an 85% yield of Pyr₁₄TFSI. H₂O solvent is used during this step in a ratio of 1:1 (%wt) g Pyr₁₄l: ml solvent.

For the ionic liquid purification, a ratio of 5:1 (%wt) Pyr₁₄TFSI:Activated carbon and 2:1 (%wt) Pyr₁₄TFSI:Aluminum Oxide is used. Overall expected yield is expected at 72%wt.

Research Connection:

There are many motivations to replace liquid electrolytes but some of the key points include how much safer solid electrolytes are, and also how much better they perform.

Materials:

Supplies

2 - 50ml round bottom flasks

1 - 50ml beaker

1 - 500 ml flask

1 - 100 ml two-necked round bottom flask
1 - 250mL vacuum filtration flask
1 - reflux condenser
4 - disposable 20mL syringes with disposable needles
1 - longer reusable metal needle
1 - PTFE syringe filter (0.45 μ m pore size)
3 - disposable glass pipettes
1 - small stir bar for 50ml flask
1 - medium stir bar for 100ml flask
1 - 65mm filtration funnel (inside width)
1 - 100ml brown glass vial
1 - 20ml glass vial
1 - thermometer
1 - silicone oil bath
1 - metallic scoop
2 - septum
3' Plastic Tubing
Balloon with septum and needle attachment
parafilm
filtration papers
plastic weigh boat
weigh papers
masking tape

Chemicals (“Abbreviations Used”)

3.605g - 1-methylpyrrolidinium (“Pyr₁”)

7.082g - 1-iodobutane (“IB”)

10.812g - Lithium bis(trifluoromethane)sulfonamide (“LiTFSI”) (should be kept under inert gas)

2.87g - Activated Carbon ("AC")

6.95g - Aluminum Oxide ("AO")

300ml - Deionized H₂O ("DIH₂O")

220ml - Ethyl Acetate ("EA") including ~200ml for washing

Hexanes for washing ("Hex")

Nitrogen Gas ("N₂")

Argon Gas ("Ar")

Equipment

1 - hot plate with magnetic stirring

1 - sonication bath

1 - water pump for vacuum filtration

1 - roto-evaporator with adjustable heat water bath

1 - analytical balance (minimum 1mg precision)

1 - vacuum oven

Procedure:

Procedure

Precursor Synthesis

1. Begin heating oil bath to 45 C on magnetic hot plate. Measure weight of a 50ml round bottom flask and tare analytical balance, then transfer empty flask to fume hood.
2. Use a disposable syringe to measure 4.51ml of Pyr1, then transfer into the 50ml round bottom flask.
3. On analytical balance measure weight of Pyr1, about 3.605g, then add 6.089g EA (6.75 to ml) to the same flask.
4. Add a stir bar and then parafilm the flask to prevent evaporation of the solvent.
5. Tare a 50ml beaker on the analytical balance, then transfer to fume hood. Using a second disposable syringe, measure 4.38ml of IB and add to the 50ml beaker.
6. On analytical balance, measure weight of IB, about 7.083g, then add 5.926g EA (6.57ml) to the same beaker.

7. Place Pyr₁:EA-containing flask into oil bath at 45 C and set stir to 200RPM for duration of reaction.
8. Remove parafilm and slowly add IB:EA solution into flask over a period of 15 minutes using the disposable syringe. Note: ~2-3ml EA used for rinsing 50 ml beaker is added to flask.
9. Cap with argon balloon and set to stir for 5 hours. Consider using some means to reduce solution's exposure to natural light in order to prevent UV-catalyzed decomposition of iodide.
10. After five hours, remove flask from heat, remembering to wash carefully with hex.
11. Isolate the product (a white powder) using vacuum filtration. Dispose of initial filtrate and then wash product with EA until filtrate is clear.
12. Store Pyr₁₄I powder in brown glass bottle, wrapped in aluminum foil to reduce light exposure.

Anionic Exchange

13. Prepare 300ml deoxygenated DI H₂O in a 500ml flask, attaching to N₂ source using the plastic tubing for one hour on a stir plate with stir bar.
14. Place weigh boat, gloves, and metal scoop into a glove box under an Ar environment to measure 10.812g of the LiTFSI. Transfer loaded weight boat out of glove box.
15. Add LiTFSI into a 50 ml beaker and cap with parafilm.
16. Take to fume hood and add a stir bar, then ~1:1 ml/g deoxygenated DI H₂O to LiTFSI. Set to stir at 400RPM for 15 minutes or until completely dissolved.
17. Add Pyr₁₄I to 100ml two necked round bottom flask, using minimal deoxygenated DI H₂O to rinse 100ml brown bottle.
18. Secure flask over magnetic stir plate.
19. Gather a septum pierced with syringe needle that can attach to the plastic tube.
20. Using a plastic tube attached to a N₂ source, insert this tube into the septum. Secure septum to flask's side neck to allow N₂ to enter the flask.
21. Set to stir lightly, then add LiTFSI:H₂O while N₂ seeps into flask. Once added, increase stir speed until solution appears turbulent, and allow to react for 1 hour at room temperature.
22. After one hour, turn off stirring and allow the mixture to settle. Settled solution should appear in two phases, a non-aqueous bottom phase, and an aqueous top phase. Both phases should appear clear, with a possible light yellow/brown coloration. The bottom phase may be turbid due to the presence of small water droplets.

23. Remove 100 ml double necked flask from magnetic hot plate. Lightly sonicate the flask if necessary to encourage coalescence of separate phases.
24. Pipette top phase into waste container. Then add ~12ml deoxygenated DI H₂O into flask.
25. Return to magnetic stir plate and set to stir for 10 minutes at a turbulent speed, then remove the flask and sonicate to encourage phase separation.
26. Repeat washing cycle (steps 22-23) six additional times for a total of seven washes.
27. After washing, remove the top aqueous phase as completely as possible. Either store the final ionic liquid product in a sealed, dry container, or proceed directly to next step.

Ionic Liquid Purification

28. Prepare an oil bath on a hot plate set to 70 C.
29. On an analytical balance, set a 50ml round bottom flask, weighed, and tared.
30. Addition of 2.87g Activated Carbon (AC) into flask
31. Pipette all ionic liquid into AC flask. Rinse two-necked round bottom flask with minimal EA, then add into AC flask. Add additional EA to bring total EA volume to 9.577g (10.6ml).
32. Secure AC Flask onto magnetic hot plate under a fume hood, adding a stir bar, and attach a water-filled reflux condenser.
33. Set to stir overnight (at least 10 hours) at 70 C and at 500 RPM. Note: Hotplate was set to 120C to reach 70 C measured in oil bath.
34. Remove flask from magnetic hot plate and wash with hex, then set aside oil bath.
35. Prepare a filtered funnel to vacuum filter solution through into a 250ml vacuum filtration flask, saving the carbon in funnel for later steps. Note: filtrate may contain some particulates, which will be removed at a later step.
36. On an analytical balance, set a 50 ml round bottom flask, weighed, and tared.
37. Addition of 6.95g Aluminum Oxide (AO) into flask, adding filtrate as well. Rinse vacuum flask with a small amount of EA.
38. Secure flask onto the magnetic hot plate, set to stir at 900 RPM at room temperature for five hours.
39. Remove flask from magnetic hot plate, and vacuum filter the AO using carbon-containing funnel from previous step.

40. Continue to vacuum filter, using 12 ml EA to wash the combined AC/AO powder and combine this washing liquid with the filtrate.
41. Draw out filtrate using disposable syringe, and inject through PTFE syringe filter into a 100 ml round bottom flask.
42. Attach flask to roto-evaporator at 40 C for about 20 minutes to remove superficial EA.
43. Transfer superficially dried ionic liquid to a 20 ml glass vial using disposable glass pipette, using slight extra EA to rinse 100ml round bottom flask and ensure complete transfer. Make sure to not overfill 20ml vial more than 2/3 full in care of roto-evaporator.
44. Attach 20ml vial to roto-evaporator at 40 C. When all EA appears to have been removed, increase temperature to 80 C for at least 10 min to ensure total removal of EA and removal of most water.
45. Place vial into vacuum oven at 80 C overnight (at least 12 hours).
46. Vent, and then fully re-evacuate the chamber in order to remove any EA or water vapor that may be present.
47. Increase heat to 120 C for 24 hours.
48. Remove from oven and store for later use.

Extensions:

what else you can do

Resources:

- provide student worksheets or readings as separate document and provide name here.

Sources:

- where to get materials- specific catalog or online sources